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㉚ References cited:
**US - A - 3 240 701
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 AGR.BIOL.CHEM. vol. 40(9), HIROSHI MAEDA:
 "Release of formaldehyde from dimethylol
 dimethyl-hydantoin, a possible antiseptic
 agent", pages 1705—1709**

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Antimicrobial compositions, method of inhibiting the growth of microorganisms and metal working fluid compositions containing these antimicrobial compositions

Background of the Invention

Antimicrobial compositions are generally added to various kinds of aqueous fluid media to reduce or inhibit the growth of microorganisms.

For instance, a wide variety of industrial aqueous fluid media are known such as metal working fluids used with metal working equipment.

The development of high speed metal cutting and grinding has resulted in the creation of lubricants containing oils and chemicals stabilized in water. These fluids impart the cooling qualities of water and the lubricating properties of oil which prolongs the life of cutting tools, reduces heat production, improves surface finish of the metal being machined, prevents warping and leaves a rust-inhibiting film of oil on the worked piece.

Normally these fluids consist of fatty or petroleum oils, soaps or synthetic based materials and additional additives such as antifoam agents, EP additives, preservatives, coupling agents and rust inhibitors. The coolants are generally marketed in the form of concentrates which are normally diluted with water by the user in ratios of 1 part oil to about 20-40 parts of water, but these ratios may vary with particular operations. The lubricant is supplied to a machine from either an individual tank containing fifty to one hundred gallons or from a large sump containing thousands of gallons which supplies many machines.

One of the problems often associated with such aqueous fluid media arises from the susceptibility of the media to the infestation and growth of various microorganisms such as bacteria and fungi (which particularly feed on the organic components thereof). The presence and buildup of such microorganisms can often lead to interference in the metal working operations as a result of the clogging of filters, buildup of slime and sludge, development of odors, rust, emulsion instability, reduced tool life and poor finish. Furthermore, in machine shops where the workers' hands necessarily come in contact with the cutting oil, usually containing finely divided sharp metal cuttings, serious problems of dermatitis may arise. These and other such similar problems have resulted in the continuing need for better antimicrobial additives for aqueous fluid media such as metal working fluids. Much effort has been devoted in recent years to controlling this problem; however, it continues to be a major annoyance which costs the metal working industry many millions of dollars each year.

A number of suggestions have been made for inhibiting the growth of bacteria in aqueous fluids such as those described in U.S. Patents No. 4,012,261; 3,591,679; 3,408,843 and 3,240,701. The use of various formaldehyde preservatives for metal working fluids including monomethylol dimethyl hydantoin and dimethylol dimethyl hydantoin has also been proposed (See Bennet, E.O., *Int. Biodeut. Bull.* 9, pages 95-110, 1973 and Maeda et al., *Agr. Biol. Chem.*, 40, 1111-2222, 1976).

Gray and Wilkinson in *J. Gen. Microbiol.*, 39, 385-399 (1965) and *J. App. Bact.*, 28, 153-164 (1965) describe the action of ethylenediaminetetraacetic acid (hereinafter sometimes referred to as "EDTA") on some bacteria. The effectiveness of such chelating agents as EDTA alone for bacterial control in aqueous systems is disputed as evidenced by U.S. Patents No. 3,240,701; 3,408,843 and 3,591,679. The antimicrobial compositions used in metal working fluids seem to suffer from one or more disadvantages including high-cost, unacceptable toxicity or low degree of effectiveness at the present state of the art.

Accordingly, it is the primary object of the present invention to provide an effective antimicrobial composition for use in an aqueous fluid medium.

A further object of the present invention is to provide an effective relatively non-toxic method for inhibiting the growth of microorganisms in an aqueous fluid medium susceptible to such growth.

These and other objects of our invention will be apparent from the discussion which follows.

Summary of the Invention

We have discovered antimicrobial compositions, suitable for inhibiting the growth of microorganisms in an aqueous fluid medium susceptible to such growth, comprising as an active ingredient a condensation product of 5,5-dimethyl hydantoin and formaldehyde (e.g., the mono- or dimethylol dimethyl hydantoin) in combination with a water-soluble chelating agent selected from ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid or the alkali metal salts thereof. A preferred antimicrobial composition formulation comprises as an active ingredient 1,3-dimethylol-5,5-dimethylhydantoin (hereinafter sometimes referred to as "DMDMH") in combination with ethylenediaminetetraacetic acid or a water-soluble salt thereof, e.g., with alkali metal or ammonium salts.

These antimicrobial compositions when added to an aqueous fluid medium provide an unexpected degree of preservation and antimicrobial activity over what one would expect from results obtained by using the hydantoin-formaldehyde condensation product or chelating agent (i.e., DMDMH, EDTA, or a salt thereof) alone.

Detailed Description of the Invention

The antimicrobial compositions of our invention thus comprise an active combination of a condensation product of 5,5-dimethyl hydantoin and formaldehyde (e.g., 1,3-dimethylol-5,5-dimethyl hydantoin, 1-methylol-5,5-dimethyl hydantoin, or 3-methylol-5,5-dimethyl hydantoin, 1,3-dimethyloxy-methylene-5,5-dimethylhydantoin and mixtures thereof) and a water-soluble chelating agent selected from ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid or the alkali metal salts thereof.

Condensation products of 5,5-dimethylhydantoin (hereinafter referred to as "DMH") and formaldehyde are well known. For example, DMDMH may be prepared as described in U.S. Patent No. 3,987,184, the entire contents of which are incorporated herein by reference. This patent describes the use of e.g., 40—75% aqueous solutions of DMDMH as a formaldehyde donor, as well as a preservative, in various pastes, soaps, skin creams, liquid shampoos and other similar preparations.

The condensation products of DMH and formaldehyde as used herein are intended to include those products wherein 1,2 or more moles of formaldehyde are condensed with each mole of DMH. Thus, the condensation products include those wherein more than 2 moles of formaldehyde may be condensed with each mole of DMH, such as, for example 1-methylol-3-methyloxy-methylene-5,5-dimethyl hydantoin and 1,3-dimethylol-oxymethylene-5,5-dimethyl hydantoin.

When added to an aqueous fluid medium, we have now found that when an antimicrobial DMH-formaldehyde condensation product such as DMDMH is used in combination with a chelating agent such as EDTA or a water-soluble EDTA salt a greatly enhanced degree of anti-microbial activity is obtained. When a chelating agent such as EDTA (or an EDTA water-insoluble salt) is used alone (at the concentration levels here involved), there is generally no significant antimicrobial activity exhibited. Further, while antimicrobial activity is observed when the DMH-formaldehyde condensation product alone is used by itself, the level of such activity is less than is desired. However, when according to the invention the chelating agent is used in combination with the DMH-formaldehyde condensation product, for reasons not entirely clear at present, the presence of the chelating agent has an unexpected effect of potentiating or greatly enhancing the antimicrobial activity of the said hydantoin-condensation component, as is more fully described below.

While ethylenediaminetetraacetic acid itself may be employed, it is preferred to use one of its water-soluble salts, such as alkali metal salts, for example the disodium salt (sometimes referred to as "EDTA diNa") or the tetra-sodium salt (sometimes referred to hereinafter as "EDTA-tNa"). The comparable potassium salts, and the ammonium salts may also be used.

The antimicrobial compositions of the present invention may thus generally be formulated to contain the active hydantoin-formaldehyde condensation product and chelating agent in a weight ratio ranging from 0.25:1 to 20:1, and preferably 1:1 to 5:1 hydantoin to chelating agent with or without additional inert liquid vehicles or dispersants, or solid extenders, or inert carriers. Most preferably, and conveniently, compositions may be formulated containing less than 5% by weight of the chelating agent.

In use these antimicrobial composition formulations may be added to an aqueous fluid medium in the form of a solid block or tablet, as a powder, or preferably as a solution.

In order to achieve practical level of inhibition of microorganism growth in the aqueous fluid medium it is necessary to include therein the active combination of a condensation product of the hydantoin (i.e., mono- or dimethylol-5,5-dimethyl hydantoin with formaldehyde and chelating agent in an amount sufficient to inhibit the growth of microorganisms. As used herein, the term inhibitive amount is to be understood as that amount of the said combination which when added to an aqueous fluid medium will acceptably inhibit the growth of microorganisms in the use of said medium. Furthermore, this level of inhibition will be greater than the additive level of inhibition one would obtain with the active hydantoin product in the absence of the chelating agent (e.g., 1 part DMDMH and 1 part EDTA is more inhibitory than 2 parts DMDMH alone).

Generally at least 500 parts of the chelating agent and at least 500 parts of active condensation product are added per million parts of the aqueous fluid medium. Thus, the chelating agent may be added in amounts ranging from 500 to 4000 parts per million (ppm) of the aqueous fluid medium. Likewise, one may suitably add from 500 to 10000 parts of active condensation product per million parts of the aqueous fluid medium. The weight ratio of condensation product and chelating agent may range suitably from 0.25:1 to 20:1 and preferably 1:1 to 5:1. Of course, with an increase in water hardness, the proportional amount of chelating agent may need to be increased to achieve desired results.

As used herein, the term aqueous fluid medium is meant to encompass water, oil in water, water in oil emulsions (including concentrates) and like compositions susceptible to the infestation and growth of microorganisms. Thus, for instance, metal working fluids or cutting oil fluids (in diluted as well as undiluted form) together with conventional additives such as corrosion inhibitors etc. are to be included.

The antimicrobial compositions may be added directly to undiluted metal working fluids. As used herein the term "metal working fluid" is intended to encompass those compositions known in the art as "metal cutting fluids", "cutting fluids", "coolants", "lubricants" "rolling oils", "drawing fluids", "mold

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release fluids", "grinding fluids" and like products used in the processing of metals as described more fully by Springborn, R. K. "Cutting and Grinding Fluids: Selection and Application," ASTME (1967) and Wilb rt J. Oeds, "Lubricants, Cutting Fluids and Coolants", Cahner's Books, the entire contents of each being incorporated herein by reference. Emulsifiable or water miscible oils are widely used in the industry. Mixed with water, they form emulsions for use in rolling, drawing, machining and grinding where the need is for both cooling and lubrication. More recently, water miscible fluids using less oil (or no oils) and based on chemicals with or without surface active agents, have provided industry with products of even greater heat conducting properties for still higher machining rates.

The following examples are offered in order to more fully illustrate the invention, but are not to be construed as limiting the scope thereof.

Experimental Procedure

Test units employed consisted of quart jars placed in rows. Above each row a metal framework was constructed to support the aeration system which consisted of aquarium valves connected together with plastic tubing. The amount of aeration of each jar unit was controlled by adjusting the valves. Capillary pipettes were employed as aerators to produce a fine stream of bubbles.

Five hundred ml of tap water (moderate hardness) was added to each jar unit. DMDMH and EDTA and DTPA were used as obtained from the manufacture and the desired amount (wt/vol or vol/vol) of each product was added to each unit along with the required amount of coolant concentrate to produce the desired oil-water ratio. (DMDMH was used as a 55% aqueous solution, identified as "DMDMH—55"). The unit was then made up to a total volume of 600 ml with additional tap water.

The jars were inoculated with a mixture of bacteria and fungi which were obtained and maintained as described in "The Deterioration of Metal Cutting Fluids," Prog. Indust. Microbiol., 13, 121—249, 1974 by E. O. Bennett, the entire contents of which are incorporated herein by reference. Over the years, samples of spoiled coolants have been obtained from many sources. These samples have been kept viable by growing them in metal working fluids. The inoculum employed in the antimicrobial tests contains these organisms and is aerated at all times. Normally, it contains between ten million to one hundred million organisms per ml.

Initially and once each week thereafter all units were inoculated with 1.0 ml of a 50—50 mixture of the two inocula (i.e., bacteria and fungi). The units were kept at ambient temperatures (27.0°C. to 28.5°C.).

The test units were studied for their microbial contents at weekly intervals by making serial dilutions of the coolant into a medium as described in the Prog. Indust. Microbiol. article noted above. Each unit was studied for so long as the counts remained below 100,000 organisms/ml. Two consecutive counts in excess of this figure at weekly intervals was considered to constitute the point of "failure", and the test was discontinued at that time.

Since the test vessels were under constant aeration, there was considerable evaporation from each jar unit. The units were calibrated at the 600 ml mark and once or twice each week distilled water was added to bring the liquid level back to this mark. Distilled water was used in order to avoid a buildup of inorganic salts which would have taken place if tap water had been employed.

Base control tests in each instance revealed that the coolants employed without the addition of chelating agent and/or hydantoin product failed within one week due to the growth of microorganisms.

Examples A and B are comparative examples; Examples 1 through 4 are illustrative embodiments of this invention.

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Example A

A series of sample jar units were prepared according to the procedure outlined above in order to ascertain the antimicrobial effect of 1,3-dimethylol-5,5-dimethyl hydantoin.

Samples tested were

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- A) 1500 ppm of 55% aqueous solution of 1,3-dimethylol-5,5-dimethylhydantoin (hereinafter sometimes referred to as "DMDMH—55");
- B) 3000 ppm DMDMH—55; and
- C) 4500 ppm DMDMH—55.

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The samples were tested with the following commercially available coolants (i.e. metal working fluids):

	<i>Coolant</i>	<i>Manufacturer</i>
60	Max Mix Coolant	Mack Co.
	Shell Emulsion	Shell Oil Co.
	Vantrol Emulsion	Van Straaten Chemical Co.
65	Sun Emulsion	Sun Oil Corp.

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	<u>Coolant</u>	<u>Manufacturer</u>
5	Norton Emulsion	Norton & Co.
10	Shamrock Emulsion Corp.	F. E. Anderson Oil & Chemical
15	DoAll Coolant	Do All Co.
20	Quaker Coolant	Quaker Chemical Corp.
25	Texaco Emulsion	Texaco Inc.
30	Irmco Emulsion	International Refining & Manufacturing Corp.
35	Polar Chip Coolant	Polar Chip Inc.
40	Shercool Coolant	Sherwin Williams Chemicals Inc.
45	Sanson Emulsion	Sanson & Sons, Inc.
50	Lusol Coolant	F. E. Anderson Oil & Chemical Corp.
55	Trim Coolant	Master Chemical Corp.
60	Cimcool 5 Star Coolant	Cincinnati Milacron Corp
65	Union Emulsion	Union Oil Corp.

The coolants were mixed with water in a ratio of 1 to 40 (coolant to water). The results are set forth in Table 1 below, wherein the time in days is recorded when the count in such test reached the level of 100,000, as described above.

Test failures in less than 60 days or less were considered likely to be unacceptable from the standpoint of potential industrial and commercial applications. Furthermore, from both a technical and statistical standpoint any data between 0 to 21 days can not be regarded as significantly different.

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TABLE 1

	Coolant	Column A	Column B	Column C
		DMDMH-55 1500 ppm	DMDMH-55 3000 ppm	DMDMH-55 4500 ppm
10	1. Max Mix Coolant	58	105*	-
15	2. Shell Emulsion	0	0	0
20	3. Vantrol Emulsion	<u>14</u>	7	0
25	4. Sun Emulsion	0	0	7
30	5. Norton Emulsion	<u>7</u>	<u>28</u>	<u>28</u>
35	6. Shamrock Emulsion	<u>28</u>	105*	105*
40	7. DoAll Coolant	<u>14</u>	7	<u>42</u>
45	8. Quaker Coolant	<u>21</u>	<u>21</u>	<u>21</u>
50	9. Texaco Emulsion	0	14	14
55	10. Imco Emulsion	0	0	0
60	11. Polar Chip Coolant	14	<u>35</u>	7
65	12. Shercool Coolant	0	21	7
70	13. Sanson Emulsion	0	0	0
75	14. Lusol Coolant	0	35	-
80	15. Trim Coolant	<u>14</u>	-	-
85	16. Climcool 5 Star Coolant	7	<u>35</u>	-
90	17. Union Emulsion	0	-	-

All testing at 1 to 40 oil to water ratio.

* Still inhibitory when taken off test.

Underlined number indicates failure due to moulds.

Example B

A series of sample jar units were prepared according to the procedure outlined above in order to ascertain the antimicrobial effect of EDTA-diNa and diethylenetriamine pentaacetic acid (pentasodium salt). Samples tested were

- A) 1000 ppm EDTA—diNa;
- B) 1500 ppm EDTA—diNa; and
- C) 1000 ppm DTPA—Na₅

The samples were tested with the same commercially available coolants (i.e., metal working fluids) used in Example .

The coolants were mixed with water in a ratio of 1 to 40 (coolant to water). The results are set forth in Table 2 below, wherein the time in days is recorded when the count in such test reached the level of 100,000, as described above.

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TABLE 2

5	Coolant	Column A	Column B	Column C
		EDTA (1000 ppm)	EDTA (1500 ppm)	DTPA (1000 ppm)
10	1. Max Mix Coolant	0	—	—
	2. Shell Emulsion	7	—	<u>105</u> *
15	3. Vantrol Emulsion	0	0	0
	4. Sun Emulsion	0	0	0
20	5. Norton Emulsion	14	14	<u>21</u>
	6. Shamrock Emulsion	7	7	0
	7. DoAll Coolant	0	0	35
25	8. Quaker Coolant	7	0	—
	9. Texaco Emulsion	7	—	—
	10. Irmco Emulsion	0	—	—
30	11. Polar Chip Coolant	0	0	—
	12. Shercool Coolant	7	7	—
	13. Sanson Emulsion	—	7	—
35	14. Lusol Coolant	—	0	—
	15. Trim Coolant	—	0	—
40	16. Cimcool 5 Star Coolant	—	7	—
	17. Union Emulsion	—	0	—

45 All testing at 1 to 40 oil to water ratio.

* Still inhibitory when taken off test.

Underlined number indicates failure due to moulds.

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Example 1

A series of sample jar units were prepared according to the procedure outlined above in order to ascertain the antimicrobial effect of EDTA—diNa and 1,3-dimethylol-5,5-dimethyl hydantoin. Samples 55 tested were

- A) 1500 ppm of EDTA—diNa;
- B) 1500 ppm of 55% aqueous solution of 1,3-dimethylol-5,5-dimethylhydantoin (hereinafter sometimes referred to as "DMDMH—55"); and
- 60 C) 1500 ppm EDTA—diNa and 1500 ppm DMDMH—55.

The samples were tested with commercially available coolants (i.e., metal working fluids).

The coolants were mixed with water in a ratio of 1 to 40 (coolant to water). The results are set forth in Table 3 below, wherein the time in days is recorded when the count in such test reached the 65 level of 100,000, as described above.

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TABLE 3

	Column A	Column B	Column C
	EDTA (1500 ppm)	DMDMH-55 1500 ppm	1500 ppm DMDMH-55 1500 ppm EDTA
10			
11	1. Vantrol Emulsion	0	<u>14</u>
12	2. Sun Emulsion	0	0
13	3. Norton Emulsion	14	<u>7</u>
14	4. Shamrock Emulsion	7	<u>28</u>
15	5. DoAll Coolant	0	<u>14</u>
16	6. Quaker Coolant	0	<u>21</u>
17	7. Polar Chip Coolant	0	14
18	8. Shercool Coolant	7	0
19	9. Sanson Emulsion	7	0
20	10. Lusol Coolant	0	0
21	11. Trim Coolant	0	<u>14</u>
22	12. Climcool 5 Star Coolant	7	7
23	13. Union Emulsion	0	0
24			49

All testing at 1 to 40 oil to water ratio.

* Still inhibitory when taken off test.

Underlined number indicates failure due to moulds.

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Example 2

A series of sample jar units were prepared according to the procedure outlined above in order to ascertain the antimicrobial effect of EDTA—diNa or tetra Na and 1,3-dimethylol-5,5-dimethyl hydantoin. Samples tested were

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- A) 500 ppm EDTA—diNa and 2500 ppm DMDMH—55; and
- B) 500 ppm EDTA—tetra Na and 2500 ppm DMDMH—55.

The samples were tested with the following commercially available coolants (i.e., metal working fluids):

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Coolant

Monroe Emulsion (Monroe Chemical Corp.)

Norton Emulsion

60

DoAll Coolant

Quaker Coolant

Polar Chip Coolant

65

Shercool Coolant

The coolants were mixed with water in a ratio of 1 to 40 (coolant to water) as above. In each instance, after a period of 105 days the units were still inhibited from the growth of bacteria and fungi.

Example 3

5 A series of sample jar units were prepared in the same manner as Examples 1—4 in order to determine the antimicrobial effect of diethylenetriamine pentaacetic acid (pentasodium salt) and DMDMH—55. Samples tested contained 2500 ppm DMDMH—55 and 500 ppm DTPA Na₅. The samples were tested with the following coolants:

10 ...

15 DoAll;

 Shercool;

15 Polar Chip;

 Quaker;

20 Norton Emulsion; and

20 Monroe Emulsion.

25 The coolants were mixed with water in a ratio of 1 to 40 (coolant to water). The results are set forth in Table 4 below, wherein the time in days is recorded when the count in such test reached the level of 100,000, as described above.

TABLE 4

30	Coolant	2500 DMDMH—55
		500 DTPA Na ₅
	Do All Coolant	105*
35	Shercool Coolant	84
	Polar Chip Coolant	105*
	Quaker Coolant	105*
40	Norton Emulsion	105*
	Monroe Emulsion	105*

45 * Still Inhibitory when taken off test.

Example 4

50 A series of sample jar units were prepared according to the procedure above in order to ascertain the antimicrobial effect of 500 ppm EDTA-dlNa and 1500 ppm DMDMH—55. The samples were tested in the same manner with the same coolants used in Example 3. The results are set forth in Table 5 below.

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TABLE 5

5	Coolant	1500 DMDMH—55
		500 EDTA Na ₂
10	DoAll Coolant	63
15	Shercool Coolant	105*
20	Polar Chip Coolant	105*
25	Quaker Coolant	105*
30	Norton Emulsion	35
35	Monroe Emulsion	105*

Notes: 1. Numbers designate days inhibition.
 2. Underlined numbers indicates test failure due to mold.
 3. * Still inhibitory when taken off test.

It will be noted that when EDTA is used in combination with DMDMH, the test results show that generally the resulting antimicrobial control was maintained for multifold periods of time longer than was observed for the same amount of either EDTA or DMDMH used alone (at equivalent concentrations).

The antimicrobial composition formulations of the present invention are particularly attractive due to the low toxicity of their components when present in the amounts indicated. Furthermore, while prior known antimicrobial formulations appear to be effective at best in only about 42% of the commercially available metal working fluids, the formulations of the present invention are more universally effective.

While the invention has been explained in relation to certain illustrative embodiments of it, it is understood that many modifications and substitutions may be made in any of the specific embodiments within the scope of the appended claims which are intended also to cover equivalents of them.

35 Claims

1. An antimicrobial composition containing a condensation product of formaldehyde and a hydantoin characterised in that (i) the hydantoin is 5,5-dimethyl hydantoin, and (ii) the composition contains a water-soluble chelating agent selected from ethylene-diaminetetraacetic acid, diethylenetriaminepentaacetic acid or the alkali metal salts thereof.
2. An antimicrobial composition as claimed in claim 1 characterized in that the hydantoin in the condensation product is selected from 1,3-dimethylol-5,5-dimethyl hydantoin; 1-mono-methylol-5,5-dimethyl hydantoin and 3-mono-methylol-5,5-dimethyl hydantoin.
3. An antimicrobial composition as claimed in claim 1 characterized in that the hydantoin in the condensation product is 1,3-dimethylol-5,5-dimethylhydantoin and the chelating agent is ethylene-diaminetetraacetic acid, or a water-soluble salt thereof.
4. An antimicrobial composition as claimed in claim 3 characterized in that the chelating agent is the disodium salt of ethylenediaminetetraacetic acid.
5. An antimicrobial composition as claimed in claim 3 characterized in that the chelating agent is the tetrasodium salt of ethylenediaminetetraacetic acid.
6. An antimicrobial composition according to any preceding claim characterized in that the ratio by weight of the condensation product to the chelating agent ranges from 0.25:1 to 20:1.
7. An antimicrobial composition as claimed in claim 6 characterized in that the ratio ranges from 1:1 to 5:1.
8. An antimicrobial composition as claimed in any preceding claim characterized in that the composition is in the form of aqueous solution.
9. A method of inhibiting the growth of microorganisms in an aqueous fluid medium susceptible to such growth by adding to said medium an inhibitory amount of a composition comprising a condensation product of a hydantoin and formaldehyde characterized in that the composition is as claimed in any preceding claim.
10. A method according to claim 9 characterized in that said composition is added to a metal working fluid.
11. A method according to claim 9 or 10 characterized in that there is added to said medium by weight at least 500 parts of the condensation product and at least 500 parts of the chelating agent per million parts of said medium.

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12. A method according to claim 11 characterized in that there is added to said medium by weight:

- (a) 500 to 10,000 parts of the condensation product, and
- (b) 500 to 4000 parts of the chelating agent per million parts of said medium.

13. A metal working fluid composition characterized in that it contains an inhibitive amount of an antimicrobial composition as claimed in any one of claims 1 to 8.

Revendications

10. 1. Composition antimicrobienne contenant un produit de condensation du formaldéhyde et d'une hydantoïne, caractérisée en ce que (i) l'hydantoïne est la 5,5-diméthylhydantoïne et (ii) la composition contient un agent séquestrant hydrosoluble choisi parmi l'acide éthylène-diamine-tétracétique, l'acide diéthylène-triamine-pentacétique ou leurs sels de métaux alcalins.
15. 2. Composition antimicrobienne selon la revendication 1, caractérisée en ce que l'hydantoïne contenue dans le produit de condensation est choisie parmi la 1,3-diméthylol-5,5-diméthylhydantoïne, la 1-monométhylol-5,5-diméthylhydantoïne et la 3-monométhylol-5,5-diméthylhydantoïne.
20. 3. Composition antimicrobienne selon la revendication 1, caractérisée en ce que l'hydantoïne contenue dans le produit de condensation est la 1,3-diméthylol-5,5-diméthylhydantoïne et l'agent séquestrant est l'acide éthylènediamine-tétracétique ou un sel hydrosoluble de cet acide.
25. 4. Composition antimicrobienne selon la revendication 3, caractérisée en ce que l'agent séquestrant est le sel disodique de l'acide éthylène-diamine-tétracétique.
5. 5. Composition antimicrobienne selon la revendication 3, caractérisée en ce que l'agent séquestrant est le sel tétrasodique de l'acide éthylènediamine-tétracétique.
25. 6. Composition antimicrobienne selon l'une quelconque des revendications qui précèdent, caractérisée en ce que le rapport en poids entre le produit de condensation et l'agent séquestrant va de 0.25:1 à 20:1.
7. Composition antimicrobienne selon la revendication 6, caractérisée en ce que le rapport va de 1:1 à 5:1.
30. 8. Composition antimicrobienne selon l'une quelconque des revendications qui précèdent, caractérisée en ce que la composition est sous la forme d'une solution aqueuse.
9. Procédé pour inhiber la croissance des microorganismes dans un milieu liquide aqueux sensible à une telle croissance par addition à ce milieu d'une proportion inhibitrice, d'une composition comprenant un produit de condensation d'une hydantoïne et du formaldéhyde, caractérisé en ce que la composition est telle que revendiquée dans l'une quelconque des revendications qui précèdent.
35. 10. Procédé selon la revendication 9, caractérisé en ce que ladite composition est ajoutée à un liquide pour le travail des métaux.
11. Procédé selon revendication 9 ou 10, caractérisé en ce que l'on ajoute audit milieu, en poids, au moins 500 parties du produit de condensation et au moins 500 parties de l'agent séquestrant par 40. million de parties dudit milieu.
12. Procédé selon la revendication 11, caractérisé en ce que l'on ajoute audit milieu, en poids:
 - (a) 500 à 10,000 parties du produit de condensation, et
 - (b) 500 à 4,000 parties de l'agent séquestrant par million de parties dudit milieu.
45. 13. Composition liquide pour le travail des métaux, caractérisée en ce qu'elle contient une proportion inhibitrice d'une composition antimicrobienne telle que revendiquée dans l'une quelconque des revendications 1 à 8.

Patentansprüche

1. Antimikrobielle Zusammensetzung, die eine Kondensationsprodukt aus Formaldehyd und einem Hydantoin enthält, dadurch gekennzeichnet, daß das Hydantoin 5,5-Dimethylhydantoin ist und die Zusammensetzung einen wasserlöslichen Chelatbildner ausgewählt aus Ethylendiamintetraessigsäure, Diethylentriaminpentaessigsäure oder deren Alkalimetallsalzen enthält.
50. 2. Antimikrobielle Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Hydantoin im Kondensationsprodukt ausgewählt ist aus 1,3-Dimethylol-5,5-dimethylhydantoin, 1-Monomethylol-5,5-dimethylhydantoin und 3-Mono-methylol-5,5-dimethylhydantoin.
55. 3. Antimikrobielle Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Hydantoin im Kondensationsprodukt 1,3-Dimethylol-5,5-dimethylhydantoin ist und der Chelatbildner Ethylen-diamintetraessigsäure oder ein wasserlösliches Salz davon ist.
4. Antimikrobielle Zusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß der Chelatbildner das Dinatriumsalz von Ethylendiamintetraessigsäure ist.
60. 5. Antimikrobielle Zusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß der Chelatbildner das Tetrannatriumsalz von Ethylendiamintetraessigsäure ist.
65. 6. Antimikrobielle Zusammensetzung nach jedem der vorang gangenen Ansprüche, dadurch gekennzeichnet, daß das Gewichtsverhältnis von Kondensationsprodukt zu Chelatbildner im Bereich von 0,25:1—20:1 liegt.

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7. Antimikrobielle Zusammensetzung nach Anspruch 6, dadurch gekennzeichnet, daß das Gewichtsverhältnis im Bereich von 1:1 bis 5:1 liegt.
8. Antimikrobielle Zusammensetzung nach jedem der vorangegangenen Ansprüche, dadurch gekennzeichnet, daß die Zusammensetzung in Form einer wässrigen Lösung vorliegt.
9. Verfahren zur Unterdrückung des Wachstums von Mikroorganismen in einem wässrigen flüssigen Medium, das anfällig für ein solches Wachstum ist, indem zu dem Medium eine wachstumunterdrückende Menge einer Zusammensetzung gegeben wird, die ein Kondensationsprodukt aus einem Hydantoin und Formaldehyd enthält, dadurch gekennzeichnet, daß die Zusammensetzung eine der in jedem der Vorangegangenen Ansprüche beanspruchten Zusammensetzungen ist.
10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß die Zusammensetzung zu einer Metallbearbeitungsflüssigkeit gegeben wird.
11. Verfahren nach Anspruch 9 oder 10, dadurch gekennzeichnet, daß 1 Million Gewichtsteilen des Mediums mindestens 500 Gewichtsteile des Kondensationsproduktes und mindestens 500 Gewichtsteile des Chelatbildners zugesetzt werden.
12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß 1 Million Gewichtsteilen des Mediums:
 - (a) 500 bis 10 000 Gewichtsteile des Kondensationsproduktes und
 - (b) 500 bis 4000 Gewichtsteile des Chelatbildners zugesetzt werden.
13. Metallbearbeitungsflüssigkeitszusammensetzung, dadurch gekennzeichnet, daß sie eine Wachstumshemmende Menge einer antimikrobiellen Zusammensetzung gemäß den Ansprüchen 1 bis 8 enthält.

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